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SYNTHESIS AND INDUSTRIAL APPLICATION OF PROTECTIVE LAYER CATALYSTS BASED ON KAOLIN FOR HYDROCLEAN INSTALLATIONS

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Abstract: *The dynamics of the accelerated formation of corrosion products of equipment in the process of obtaining diesel and oil fractions from sour oil with a high concentration of resinous asphaltic substances and derivatives of petroleum acids are investigated in this work. The following experimental data is obtained: the genesis of the phase composition during the synthesis of granules of the protective layer from kaolin phosphate mass, followed by their modification with* Ni^{2+} *ions in order to control the surface acidity and the hydrogenating function focused on the conversion of reactive alkenes. The mechanism and conditions for the formation of samples of catalysts of the protective layer of the core type containing the weight of 2.5%, are discussed. NiO in the surface layer, and 5 times less in the inner part of the granules which consist of particles of clay mineral cemented Al* $(H_2PO_4)_2$*, as well as other products of dissolution of kaolinite and hydromica with phosphoric acid, are also studied. The results of the study of the efficiency of removal of corrosive iron and impurity elements of petroleum origin in granules of the developed protective layer are presented. It has been established that the use of granules of a protective layer in optimal shape and size, together with a reduced tendency to form a solid crust of sediments, limited the increase in pressure drop on the layer of CoMo catalyst of hydrofining oil distillates and the deasphalted vacuum residue of high-sulfur tarry oil.*

Keywords: *protective layer, kaolin phosphate mass, used catalyst, hydrocleaning, crust type catalyst, pressure dropping.*
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Introduction

At present there is a tendency to extract oil with high sulfur content, resinous asphaltenic substances and organometallic compounds along with a reduced yield of light distillates [1,2] due to the continuous increase of demand for environmentally clean fuel and oil fractions. Processing of problematic raw materials makes it important to develop protective layers taking into account its specificity [3], features of the adopted technology, economic feasibility of regeneration for reuse [4-6] and recovery of used catalysts with extraction of valuable metals [7-8]. During the execution of the schemes for deep processing of heavy hydrocarbon raw materials and radical reconstruction of existing plants, production of petroleum products using the existing technology continued at a number of enterprises with high level of depreciation of fixed assets which naturally has a negative effect on the process. Not planned transition from one hydrocarbon to another one during the operation of a package of catalysts, designed for certain indicators, arises a number of problems even on new type installations and requires the adoption of emergency measures [9]. This article is devoted to the technology for protective layers preparation from a cheap clay mineral and consideration of the experience of their industrial use with an emphasis on the rational application of used CoMo hydrofining catalyst.

Experimental part

1.1. *Synthesis of samples of the protective layer*. The protective layer based on kaolin phosphate cement mass (hereinafter referred to as KPC) intended for the installation of hydrofining of diesel fuel with high content of corrosion products was formed in the form of Raschig rings (D=15 mm, d=8-10 mm, h=14-16 mm) from the kaolin phosphate mass. The kaolin phosphate mass is obtained by mixing kaolin of the Angren deposit with phosphoric acid (17: 1) and further by heat treatment at a temperature not higher than 723 K. The mineral composition of raw material (% weight): Al_2O_3 14-27; SiO_2 52-73; Fe_2O_3 0.5 - 3.9; TiO_2 0.3 - 0.9; CaO 0.11 -2.0; MgO from 0.10 up to 0.90; K_2O 0.02-0.60; Na_2O 0.08 - 0.11; SO_3 0.1 up to 0.4. In diffractograms the rock-forming mineral of the used kaolin – $Al_2[Si_2O_5](OH)_4$ (kaolinite) manifested itself by a series of reflections from interplanar distances d (here and further d in angstroms Å) with % intensity in parentheses: d = 7.18-7.14 (38); 4.46(23); 3.57(48) and 2.6-2.2 (2-10) Å. Impurity crystals of quartz - SiO_2 corresponded to the line with d = 4.26 (22); 3.34(100); 2.45-2.46(11); 1.81-1.82(18-20); 1.54-1.55(16) and 1.38-1.37(17) Å. In the composition of the kaolin, hydromuscovite - $K_{<1}Al_2[(Al, Si)_4O_{10}]\cdot(OH)_2\cdot nH_2O$ with d=9.98(5), 4.97(4), 4.47(5), 4.11(1), 3.31(4), 2.98(2), 2.84(1), 2.56(4), 2.44(2), 2.38(3), 2.24(3), 2.18(2), 2.11(3), 1.98(4), 1.65(3), 1.64(3), 1.50(5), 1.38(2), 1.29(3) and 1.24(2) Å, as well as other hydromica and impurity minerals concentrated in the thinnest clay fraction. Due to the interaction of kaolinite and impurity hydromica with phosphoric acid, a plastic mass was formed and then hardened at a room temperature. The finished KPC granules calcined at 723 K, had mechanical crush strength at the end of 43-44 MPa, a pore volume with a radius of 10^3 nm — less than 0.1 cm^3/g, and a radius of 3-4 nm — 0.13 cm^3/g.

1.2. A nickel-containing protective layer of the crust type (hereinafter referred to as PL-30) with increased porosity and a rough surface was developed specifically to prevent the rapid growth of pressure drop in hydrofining oil reactors at a hydrogen pressure not exceeding 3 MPa, where it is impossible to perform periodic regeneration of catalysts directly in the reactor. PL-30 (D=30 mm, d=10 mm, h=30-31mm with protrusions of 1 mm along the generatrix) was prepared on the basis of kaolin phosphate mass with a burnable additive. Nickel nitrate on the calcined granules was applied by impregnation with pH=6.2 aqueous solution. The finished granules PL-30 had mechanical crush strength at the end 36-38 MPa, pore volume with radius 10^4-10^5 nm - 0.04 cm^3/g and radius 5-6 nm - 0.14 cm^3/g.

1.3. Methods of investigation. The phase composition of used catalysts and deposits was studied on a Dron-3 diffractometer using CuK_{α} radiation. The macro level distribution of elements in the carrier grain was studied on JXA 8800R “Super probe” scanning electron probe microanalyzer (Jeol, Japan). The porous characteristics and specific surface area of the carriers and catalysts were determined on “Carlo Erba” porosimeter. IR transmittance spectra were obtained on SP-3 PYE UNICAM and electronic spectra on Hitachi-330. The content of Co, Ni, Mo, V, Fe in catalysts, sediment composition and hydrocarbon fractions, following the corresponding sample processing, was determined by atomic absorption spectroscopy on SP 9 PYE UNICAM. Testing of changes in the catalytic properties of fresh, used and regenerated catalysts was carried out at the pilot set during the hydrocleaning of the deasphalted residue (sulfur content is 1.3% weight) at a temperature of 573 K, a pressure of 3 MPa and hydrogen:raw materials ratio = 1:250.

Results and discussion

2.1. Analysis of the role of the developed protective layer based on kaolin phosphate mass in the hydrocleaning of diesel distillate

As for the modern hydrocleaning of diesel fractions (HDF), the rate of pressure drop increased sharply due to the formation of a dense crust of sediments with high concentration of iron compounds between ceramic balls of the frontal layer after the transition to high-sulfur raw materials [9]. This led to the early decommissioning of a part of imported Al-Mo catalyst of protective layer characterized by dense packing of rings and low efficiency in trapping corrosive iron. To ensure the stability of the process and increase the efficiency of the multilayer catalyst system, it was necessary to adapt it to specific raw materials [3]. By step-by-step analysis of changes in the chemical composition in the process of distillation of oil to be processed, we found out an abnormal increase in the concentration of iron compounds in the distillation products in comparison with other metals in the oil composition. Uzbekistan's high-sulfur tarry oil with up to 33% weight of resinous asphaltenic substances to be processed differed in their relatively low content (10^{-4} % weight) of typical catalytic poisons: V - 4.8-26.5, Ni - 4.5-7.9 and Fe - 1.2-1.3 but increased concentration of calcium Ca - 39.4-45.8 and petroleum acids. The diesel fraction obtained from this raw material, when fed to the hydrofining reactor, besides 40-50 mg/l of suspended corrosion products, included free naphthenic acids (acid amount 0.06-0.13 mg KOH/g), as well as their lime and alkali salts. At temperatures above 523 K, the salts of naphthenic acids were intensively decomposed during the preheating of the raw materials in heat exchangers, and the released, free naphthenic acids with high surface activity corroded metal pipes and equipment. Thermal regeneration could not fundamentally solve the problem of pressure drop increase, since the crust of sediments consisted of 90–95% of γ-$FeO(OH)$, FeO, Fe_2O_3, Fe^o mixture and continued resisting to the flow of reactants after burning of organic substances. The situation with pressure drop improved significantly when replacing (after the next cycle of oxidative regeneration) tightly packed ceramic balls to the hollow cylinders of the protective layer KPC [10]. The optimal shape and moderate (pK_a = 2.5-3.0) surface acidity of the KPC granules prevented the corrosion effectively. Therefore, the increase in pressure drop decreased from 0.01 MPa per day to 0.004 MPa per month under the maximum permissible value for this installation of HDF - 0.5 MPa.

After five years of operation the analysis of used granules which were selected from a three-layer package of Al-Mo, Al-Ni-Mo and Al-Co-Mo and KPC catalysts, showed the following: ablation of active components (% weight of content in fresh catalysts) 6–11 Mo, 5–9 Co, 7–10 Ni, and irreversible changes in texture under the prolonged exposure of temperature 633–653 K proved to be predominant factors for fall in the activity of hydrodesulfurization catalysts for diesel distillate. The number of metal deposits formed on the catalysts and KPC during the processing of raw materials with iodine amount 5 containing (% weight): 1.06 S, 0.25 N, 14.5 of polycyclic aromatics were within the range (10^{-4} % weight): 0-0.02V, 0.02-0.03Ni, 0-0.23Ca, 0.1-0.8Fe. The main difference from the published data on similar processes was the increased clogging of pores of the used catalysts with iron and calcium compounds under the minimal poisoning of the V and Ni active centers. Co-Mo composition of the catalyst used for 5-7 years in hydrocleaning process of distillate fractions was (% weight): 47 Al, 5.1 Mo, 1.8 Co, 0.3 Fe [7], similar changes were observed during the operation of fresh NiMo catalyst (% weight): 7.71 Mo; 3.2 Ni; Co 0.04, and the composition of the used samples was within the range (%): 6.6-6.9 Mo, 2.95-2.81 Ni, 0.04 Co, 0.07-0.35 Fe, 0-0.46 Na, 0.007-0.01 Pb, 0.002-0.0035 As [4]. The positive effect of the protective layer was the contact of resinous compounds and substances of unsaturated nature in the composition of the raw diesel distillate with the moderately acidic surface of the KPC, and this contact was limited by the formation of a sticky layer without provoking the polymerization of unstable processing products. Dissolved corrosion products at a temperature of 633-673 K intensively absorbed hydrogen sulfide with the formation of bulk insoluble deposits. The adhesive surface of the KPC retained FeS_{1-x} well, and the wide channels stabilized the pressure drop in the HDF reactor.

2.2. The problems arising in the processing of high-boiling oil fractions under reduced pressure of hydrogen

Previously, during the processing of oil fractions with moderate sulfur content (up to 1%) and petroleum acids, it was repeatedly (1-2 times a year) that it was necessary to stop the hydrofining reactor as the maximum allowable pressure drop was reached on the Co-Mo layer of the catalyst. The rise in resistance to the raw material flow was due to the formation of dense agglomerate of highly coked catalyst, chips, dust and coke-like deposits under a layer of (D = 20 mm, d = 15 mm) of inert ceramics. The design of the existing unit for hydrofining oil fractions made it no possible to regenerate the deactivated catalyst directly in the reactor. Therefore, the catalyst was cooled in nitrogen flow to minimize temperature flashes, the distribution ceramic rings were removed and cleaned of deposits buildup, and then the layer of Co-Mo sinter agglomerate of the catalyst with compaction and corrosion products was broken. Large fragments of agglomerate and small fragments of the catalyst were removed, and sifting of whole granules (more than 3 mm) returned to the reactor. Then, the required amount of fresh catalyst was recharged and the purified ceramic rings placed. Thus, the bulk of the Co-Mo catalyst was operated for 5 years without regeneration and mechanical cleaning of coke-like deposits. Therefore, even the least clogged granules in the lower part of the reactor contained (wt%) as follows: 0.43Fe, 2.05 Na and Ca, 0.06 Ni (Table 1). The contact of an active fresh catalyst in a zone of relatively high temperatures and raw materials with an admixture of unsaturated compounds initiated the formation of seal products in the upper layer which was accompanied by an accelerated increase in pressure drop. The content of "dry coke" in the granules of the upper layer formed within six months after the last addition of fresh Co-Mo catalyst was 16.2-14.8%, and the average total amount of precipitated metals reached 15% by weight. As a result, about 37% of the catalyst used was found unsuitable for regeneration and sent for recuperation to recover valuable metals (Table 1).

Owing to the need in alternate processing of II-III of the oil fraction containing (% by weight): 0.87-1.15 sulfur, 0.3-0.5 resinous asphaltene substances, 1-2 naphthenic acids and deasphalted vacuum distillation residue (1.2-1.83% by sulfur weight) at a pressure of less than 3 MPa, it became necessary to develop a technology for preparing a special protective layer. Since laboratory studies have shown that under conditions of low hydrogen pressure at acid centers, KPC with a $pKa \geq 2$, intensive gum formation occurred with deterioration in the color of oil distillate by 1.3-2.2, and deasphlted oil for 1.8-3.3 unit of DOC (dark oil color). In addition, tar deasphalting was maximum with respect to metal compounds in the composition of asphaltenes and porphyrin complexes, but less effective in cleaning from high-boiling cyclopentane carboxylic and other petroleum acids, as well as their salts. Therefore, deasphalted oil was highly enriched with corrosion products of the equipment.

Table 1. Changes in the elemental composition and properties of Co-Mo catalyst in industrial operation without a protective layer in hydrocleaning process of oils (pressure 3.0-3.1 MPa, temperature 320-330 °C)

	Scraping the depo-sits on the granules	Fresh catalyst	For recuperation (37%)		For regeneration (63%)	
			Used	Thermore generated	Used	Thermoregenerated
Chemical composition; %						
Al	2.3-3.8	40.7	18.1-22.7	23.2-31.5	29.4-34.7	35.8-36.7
Mo	1.2-1.7	8.19	3.55-3.69	7.2-7.4	3.95-5.1	7.13-8.03
Co	0.2-0.5	3.37	2.49-2.56	3.22-3.33	2.55-2.6	3.31-3.35
Ni	0.1-0.3	-	0.09-0.11	0.12-0.15	0.02-0.1	0.06-0.12
S	11-13.7	-	23.1-20.5	7.6-8.3	11.3-15.8	0.07-1.3
Na	0.1-0.2	0.3	0.49-0.52	0.58-0.71	0.2-0.3	0.27-0.35
Ca	0.8-0.3	0.02	7.5-9.8	10.2-13.1	0.94-2.41	1.78-2.52

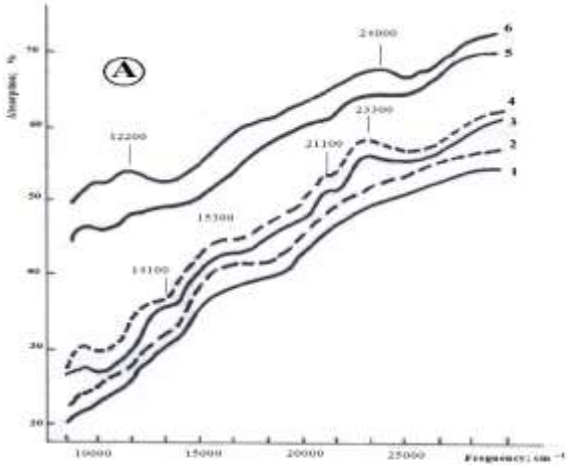
Fe	13-19.1	0.05	5.27-5.43	6.8-7.3	0.35-0.41	0.43-0.58
V	0.0-0.2	-	0.33-0.28	0.23-0.46	0.00-0.01	0.00-0.01
P	0.1-0.3	-	0.02-0.22	0.03-0.31	0.00-0.12	0.13-0.15
Si	0.3-0.7	0.04	0.04-1.08	0.42-1.49	0.93-0.05	0.07-1.2
Cl	0.2-0.6	-	2.16-2.71	2.36-3.82	0.00-0.03	0.04-0.05
Cr	0.0-0.0	-	0.0 -0.01	0.0-0.25	0.00	0.00
Cu	0.0-0.1	-	0.0 -0.02	0.1-0.5	0.00	0.00
C	32-34	-	14.8-16.2	1.8-4.3	15.2-16.8	0.2-2.1
N	0.1-0.2	-	0.07-0.38	-	0.11-0.23	-
H	4.8-5.4	-	1.8-2.3	-	3.3-4.2	-
Extractable straight-run gasoline, g/100 g sample						
Resins	7.6	-	8.4	-	9.6	-
Asphaltenes	5.2	-	4.9	-	3.8	-
Physical properties (γ- Bulk density, G- Abrasion in 15 minutes, V- Pore volume)						
S_{sp}.;m^2/g	-	190	58.6	76.4	78.2	126.4
γ; t/m^3	-	0.71	1.12	0.93	0.97	0.77
G.; %	-	11.1	37.8-42.3	26.2-40.8	13.4-18.3	12.2-15.7
V; sm^3/g	-	0.54	0.21-0. 28	0.33-0.36	0.30-0.31	0.45-0.46
The degree of sulfur removal (% wt.) during testing Co-Mo catalyst						
-	-	61,1	24.2	29.4	38.6	44.8

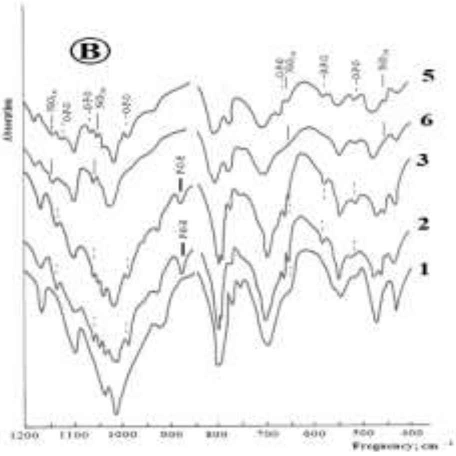
According to systematic analysis, the content of Ca, Ni, and V in the residue of vacuum distillation — tar, increased from 8.3–11.2 times as compared with the initial petroleum, and iron compounds — 93-102 times. The concentration of typical metals found in the deasphalted hydrocarbon feedstock before it entered the hydrotreating reactor heat exchanger was (10–4% by weight): ≤ 0.3 V, 1.2–1.7 Ni, 2.2–5.4 Fe, 7–15 Ca. But when the raw material was heated to 573-603 K, additional formation of corrosion products was observed in the tubes of the heat exchanger before entering the reactor. Deasphalted oil, in addition to 1-5% by weight of resinous asphaltenic substances, of which up to 30% was coxogenic asphaltenes, contained substances of unsaturated nature (iodine number 0.4–0.8 g J2 / 100 g), which had high reactivity in the formation of compaction products that stimulated reactor plugging. The hydrodesulfurization of heavy petroleum feedstock in a reactor with a stationary Co-Mo layer of catalyst proceeded virtually in three-phase system, since granules of the catalytically active substance were in contact with a two-phase flow: gas - liquid. In the downstream direction of the processed raw material, the liquid phase existed in the form of droplets, separate jets and films on the surface of solid granules; at the same time the gas flow was evenly distributed over the cross section of the reactor. It is known that these conditions are favorable for the absorption of hydrogen by a hydrocarbon liquid with its subsequent penetration through the liquid phase film to the outer surface of the granules and diffusion through the pores filled with liquid to the active sites of the catalyst. In the absence of a protective layer, the products of corrosion and the supramolecular structures of asphaltenes present in the petroleum residues significantly hampered the adsorption of hydrogen.Due to multipoint adsorption, they were firmly retained on the external surface of the granules and, upon reaching the critical concentration, they sharply worsened the diffusion processes and stimulated coke formation at acid sites in the pores of the Co-Mo catalyst. Taking into account all these factors, it can be stated that to ensure favorable hydrodynamic conditions during the processing of viscous raw materials, large granules of a protective layer with a moderate size of through holes and little active in compaction reactions are necessary.

2.3. Formation of crust type protective layer - ZS -30 and analysis of industrial run results.

The specificity of the use of kaolin-phosphate cement mass for the synthesis of granules is determined by the mechanism of reactions occurring in the process of its setting and calcination. Binding (cementing) properties were formed at the stage of mixing the components during the reaction of phosphoric acid with particles of kaolinite and hydromica due to the formation of aluminophosphates. In the diffractogram of the dried sample, the lines of quartz were preserved, the intensity of the lines characteristic for kaolinite was reduced, and hydromica was not practically manifest. Instead, a powerful halo was formed in the region d = 7.8-2.4 Å, against which a set of lines appeared (d in Å, the intensity in% is shown in parentheses) corresponding to various modifications of Al $(H_2PO_4)_2$: d = 7.71 (35); 4.08 (17); 3.67 (12), 7.50 (21); 6.03 (9); 3.50 (18) Å and d = 5.97 (11), 4.16 (7); 3.55 (32) Å, Si $(HPO_4)_2$: d = 7.36 (38); 3.42 (36); 2.43 (8) Å, $SiH_2(PO_4)_2$: d = 7.32 (10), 3.82 (6), 3.46 (4) Å and individual lines that could be attributed to H_3PO_4: d = 3.70 (6); 3.01 (4); 2.88 (7) Å and $H_4P_2O_7$: d = 4.72 (5); 4.30 (4); 3.99 (9); 3.51 (7); 3.18 (4); 3.11 (4) Å. At the stage of wilting the molded granules, large particles of clay minerals in the kaolin composition undissolved in H_3PO_4 were firmly glued together by acid aluminum phosphates, but as a result of migration of the phosphoric acid solution and shrinkage during drying, cracking of thick-walled granules occurred, in contrast to thin-walled CPC. This problem was solved by a burnable additive to improve the rheological properties of the kaolin-phosphate mass and increase porosity. During calcination, the dissolution of the kaolin particles continued, respectively, the size of the kaolinite crystals decreased, and the hydromica was almost completely destroyed. In parallel, during the migration of the liquid phase, acid aluminum phosphates were converted to tertiary ones, which were concentrated closer to the surface, along with sparingly soluble, weak-acid tertiary phosphates of alkaline-earth metals and iron. According to elemental analysis, the content of aluminum oxide in the volume of granules reached 30.7 wt. %, while the surface layer of 0.1-0.3 mm thick was depleted of aluminum oxide, where the concentration of aluminum, in terms of Al_2O_3, was only 17-18 wt.%. The amorphous silica formed during the destruction of minerals was preferably concentrated on the granules surface together with the tertiary phosphates of impurity metals. On the diffractogram of the inner part of the granules, the intense lines from initial crystals of quartz and kaolinite partially overlapped the lines of the binder — acid phosphates of Al (H_2PO_4) 2: d = 5.97 (4); 4.16 (35); 3.55 (38) Å, AlH_3 (PO_4) $_23H_2O$: d = 7.12 (37); 4.52 (7); 3.56 (40) Å, $CaHPO_4$: d = 3.37 (42); 3.35 (96); 2.96 (7) E, $Ca(H_2PO_4)$ 2: d = 3.63 (17); 3.61 (15); 3.49 (11) Å, Fe $(PO_3)_3$: d = 5.53 (3); 4.44 (20); 3.93 (9); 3.74 (13); 3.67 (11); 3.50 (24) Å. On the diffractogram of the scraping from the external surface of the granules, were identified as SiP_2O_7: d = 3.74 (9); 3.05 (7) Å, as a mixture of poorly crystallized tertiary phosphates of $AlPO_4$: d = 3.36 (5); 2.23 (5); 2.18 (6); 1.83 (5); 1.71 (3); 1.59 (2); 1.55 (4); 1.48 (2); 1.39 (2) Å, Al_3 $(PO_4)_2(OH)_3$ $9H_2O$: d = 9.8 (2); 9.1 (4); 5.43 (3); 5.28 (3); 5.10 (2); 4.61 (11); 3.93 (15); 3.48 (25); 3.38 (27); 3.17 (12) Å, $Ca_3(PO_4)_2$: d = 3.91 (13); 3.21 (9); 2.89 (8); 2.62 (3) Å, $FePO_4$: d = 4.39 (21); (3.45 (18); 2.53 (11) Å, Fe $(PO_3)_3$: d = 4.44 (23); 3.74 (22); 3.50 (17) Å against the background of two halos of amorphous silica in the range d = 22-6; 4.9-2.7 Å. In the scraping from the granules of the well prepared ZS-30, in addition, the lines from NiO d = 2.40 (5); 2.08 (7); 1.47 (4); 1.26 (2) Å were observed. The enrichment of the surface layer with nickel in oxide form which occurred during the modification, follows from the similarity of the diffuse reflectance electronic spectra with the spectrum of the NiO_{1+x} phase but not of the Ni^{2+} ions in the salt composition (Figure 1). The weakness of the reflections of the new growths is explained by the low concentration of individual grains on the surface, as well as by the polymorphism of the reaction products occurring during the synthesis of ZS-30. The predominance of acid phosphates in the volume of the granules of ZS-30 was confirmed by the presence of an intense band of 872–875 cm^{-1}

from the absorption of P-O-H bonds in the HPO_4^{2-} and $H_2PO_4^-$ groups, except for a set of bands in the valence region (1130-890 cm^{-1}) and deformation (660-525 cm^{-1}) of vibrations of O – P – O bonds in molecules of both tertiary and acid phosphates (Fig. B).





The heterogeneity of the phase composition predetermined the production of granules of the “crust” type, since the low solubility of surface phosphates impeded the penetration of nickel nitrate solution with pH = 5.2-6.0 into the volume, and a local increase in pH to 6.7-7.0, caused by the hydrolysis of calcium phosphates contributed to the precipitation of nickel hydroxide. After heat treatment, a layer about 0.2 mm thick was formed with a NiO concentration of 2.4–2.6 wt. %, able to hydrogenate C = C bonds in the open hydrocarbon chain and weak acid sites with a pK_a from +3.8 to +6.8, the concentration of which did not exceed 0.13 and 0.16 mg-eq / g. At the depth of the granules, the concentration of NiO was 0.1 wt. % with a total content of nickel oxide in the composition of the finished sample ZS-30 - 0.5 wt.%. At the depth of the granules, the concentration of NiO was 0.1 wt. % with a total content of nickel oxide in the composition of the finished sample at ZS-30 - 0.5 wt.%. In the volume of the granules, the strength of the acid sites due to aluminum phosphate reached $pK_a \leq -3$ (0.015 mg eq / g), and the number of weaker pK_a sites from –3 to +1.5 and from +1.5 to +3.8 was 0.14 and 0.20 mg eq / g, respectively. Under laboratory conditions to reduce the iodine number and color index, it was proved that the presence of “NiO crust” with $Ni_3(PO_4)_2$ impurity on the granules ZS-30 ensured the hydrogenation of the most reactive compounds with unsaturated bond in the residual oil and reduced resinification.

In an industrial reactor, the use of a protective layer of the ZS-30 substantially reduced the negative impact of harmful components of the raw materials and improved conditions of mass transfer. Sufficient free volume between the granules of the upper layer made it possible to conduct the process with a rational feed rate of raw materials that prevented the formation of stagnant zones contributing to local coke formation. The low linear velocity of the gas feed stream in the internal cavities and gaps between the protrusions on the outer surface of the contacting granules ZS-30 created favorable conditions for sedimentation of impurity particles and limited their penetration into the Co-Mo layer of the catalyst. Co-Mo catalyst complex with a protective layer of ZS-30 functioned in an industrial reactor of the G-24 unit for 6 years without interrupting the alternating hydrotreatment process of fraction III of distillate and deasphalted vacuum distillation residue due to a sharp decrease in the blockage of catalytic loading with sediments. At the last stage of operation, the pressure drop in the reactor did not exceed the permissible value. After the completion of the work cycle in the unloaded granules, individual agglomerates of various sizes were found to consist of ZS-30 or Co-Mo catalyst with coke-forming deposits, but there was no solid crust. The fraction of crumbs and fragments of catalyst with a size of less than 3 mm did not exceed 7 wt.%, and no crushed ZS-30 granules were detected. Statistical processing of the results arising from comparison of the mechanical strength of representative samples of whole granules and fragments of a Co-Mo catalyst with content of metals deposited in the pores revealed an unambiguous antibate dependence of the strength characteristics upon the amount of accumulated calcium. It is the pronounced ability of the ZS-30 to accumulate calcium (Table 2) that led to the smaller amount of crumbs and granules with reduced strength that are non-regenerable. As for granules of Co-Mo catalyst directly under the ZS-30 over a 6-year period of operation formed (in wt.%) 17.5-15.2 "dry coke", the total content of precipitated metals was within 6.6-11.8, including accumulated 6-10.6 Na, Ca and Fe.

Comparison of the analysis results of the deposits fragments on the granules of the upper layer of the Co-Mo catalyst and ZS-30 indicated slight fluctuations in the concentration of V, Ni and other metals during both cycles of operation. De-waxed oil distillates were alternately applied to hydrotreating (T_{boil} = 623-773 K, color 4.5-8.0 CNT units, sulfur content 0.93-1.05 wt.%) and deasphalted residue (T_{boil} = 773-863 K, colour> 8.0 CNT units, the sulfur content is 1.22-1.48 wt.%). As for the Co-Mo catalyst used in the presence of ZS-30, a lower degree of interaction of active components with the carrier was detected (3.9 wt.% $CoAl_2O_4$). The composition of the granules used without the application of a protective layer contained an average of 6.8 wt.% CoAl2O4, which is caused by a shor-term temperature increase during forced shutdowns for maintenance work to remove a layer of dense agglomerate from heavily clogged granules associated with deposits of "dry coke" and tar-asphaltenic substances, adding fresh Co-Mo catalyst and starting the reactor.

Table 2. Changes in the elemental composition and properties of Co-Mo catalyst in industrial operation with a protective layer in hydrocleaning process of oils (pressure 3.0-3.1 MPa, temperature 320-330 °C)

	Protective layer - ZC-30		For recuperation (13 %)		For regeneration (83%)	
	Fresh	Used/ scraping	Used	Thermoregenerated	Used	Thermoregenerated
Chemical composition; %						
Al	11.5	8.52/0.3	17.7-25.7	26.5-32.4	26.9- 28.2	36.4-38.2
Mo	0	0/0	2.8-3.9	3.91-5.42	4.61-5.33	7.73-8.02
Co	0	0/0	1.8-1.9	2.52-2.64	2.55-2.57	3.35-3.38
Ni	0.5	0.64/0.72	0.12-0.18	0.17-0.23	0.05-0.16	0.00-0.17
S	0.55	0.97/10.8	19.8-22.9	7.2-9.8	13.8-16.2	0.05-1.3
Na	0	2.37/2.5	0.21-0.63	0.31-0.87	0.16-0.4	0.18-0.35
Ca	3.5	4.82/2.5	3.58-5.22	5.0-7.3	0.44-1.33	1.17-2.97
Fe	1.69	5.92/15.9	2.23-4.72	3.4-6.7	0.26-0.37	0.32-0.49
V	0	0/0.008	0.13-0.43	0.28-0.62	0.00-0.01	0.00-0.01
P	4.8	4.3/0.07	0.28-0.32	0.16-0.53	0.13-0.19	0.13-0.14
Si	22.5	19.8/6.2	2.07-3.47	3.32-4.93	0.07-1.83	0.08-1.92
Cl	0	0.94/0.5	1.35-2.92	1.72-4.13	0.02-0.05	0.01-0.08
Cr	0.16	0.18/2.9	0.00-0.01	0.00-0.02	0.00	0.00
Zn	0	0.05/0	0.00-0.03	0.02-0.05	0.00	0.00

Mg	1.05	0.98/0	0.03-0.05	0.04-0.1	0.00-0.03	0.00
Ti	0.27	0.15/0.02	0.00-0.13	0.05-0.19	0.00-0.04	0.00
Cu	0	0.2/0.3	0.27-0.38	0.19-0.43	0.00-0.01	0.00-0.01
C	0	8.8/27.3	15.2-17.5	8.3-9.7	14.5-16.9	0.2-2.3
N		0.4/0.0	0.11-0.43	-	0.32-0.58	-
H		5.9/3.0	1.9-2.1	-	2.7-3.3	-
Extractable straight-run gasoline, g/100 g sample						
Resins	0	2.7/0.7	8.8	-	10.3	-
Asphaltenes	0	4.8/8.9	5.2	-	4.1	-
Physical properties (γ- Bulk density, G- Abrasion in 15 minutes, V- Pore volume)						
$S_{sp.}$; m^2/g	32	0.1/0.2	28.4-36.6	53.2-63.7	97.8-100	138-141
γ; t/m^3	0.98-1.03	1.17-1.28	1.12-1.15	0.92-0.95	0.83-0.86	0.73-0.75
G.; %	1.1	7	18.3-38.5	16.6-37.4	12.8-17.1	11.8-14.8
V; sm^3/g	0.18	0.03	0.11-0.15	0.29-0.32	0.26-0.28	0.49-0.51
The degree of sulfur removal (% wt.) during testing Co-Mo catalyst						
-	-	-	29.2	33.1	44.0	51.5

Co-Mo catalysts after the completion of each operation cycles and jigging of heavily contaminated and destroyed granules were subjected to thermo-oxidative regeneration with water vapor in a rotating laboratory furnace.

Testing of catalytic properties (Tables 1 and 2) showed that the degree of deactivation of the bulk of the Co-Mo catalyst in the case of ZS-30 was slightly lower than –27.2 instead of 33.4%, and the degree of recovery of the hydrodesulfurization function under optimal conditions, on the contrary, was above 93.8% other than when operating without a protective layer.

Conclusions

1. Replacing ceramic balls with rings based on kaolin phosphate mass with a large free volume for sedimentation of mechanical impurity of corrosive iron made it possible to slow down the progressive increase in pressure drop in the hydrotreating reactor of diesel fractions during the transition to less favorable oil stock.
2. When hydrotreating a deasphalted oil residue with a low content of typical catalytic poisons V and Ni, the decisive factor determining the degree of deactivation of the catalyst and the expediency of its reuse is protection against corrosion products.
3. Protective function of the new catalyst of the protective layer ZS-30 is due to the combination of moderate surface acidity limited by the hydrogenating activity of the NiO surface phase with the presence of very wide pores for the accumulation of corrosive iron and calcium salts.

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СИНТЕЗ И ПРОМЫШЛЕННОЕ ПРИМЕНЕНИЕ КАТАЛИЗАТОРОВ ЗАЩИТНОГО СЛОЯ НА ОСНОВЕ КАОЛИНА ДЛЯ УСТАНОВОК ГИДРООЧИСТКИ

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Получены экспериментальные данные по генезису фазового состава в процессе синтеза гранул защитного слоя из каолинфосфатной массы, с последующим их модифицированием ионами Ni^{2+} *для регулирования поверхностной кислотности и гидрирующей функции, ориентированной на превращение реакционно-способных алкенов. Обсужден механизм и условия формирования образцов катализаторов защитного слоя корочного типа, содержащих 2.5 % вес. NiO в поверхностном слое, и в 5 раз меньше во внутренней части гранул, состоящей из частиц глинистого минерала сцементированных* $Al(H_2PO_4)_2$*, а также другими продуктами растворения каолинита и гидрослюд фосфорной кислотой.*

Ключевые слова: *защитный слой, каолинфосфатная масса, отработанные катализаторы гидроочистки, катализаторы корочного типа, перепад давления.*

HİDROTƏMİZLƏMƏ QURĞULARI ÜÇÜN KAOLİN ƏSASINDA MÜDAFİƏ LAYLI KATALİZATORLARIN SİNTEZİ VƏ TƏTBİQİ

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Kaolin əsasında müdafiə laylı katalizatorların faza tərkibinin genezisinə aid eksperimental məlumatlar alınıb. Alkenlərin çevrilməsi üçün nəzərdə tutulan bu katalizatorların turşuluğunu və hidridləşmə qabiliyyətini tənzim etmək üçün onlar Ni^{2+} ionları ilə modifikasiya olunub. Bu tip katalizatorların formalaşmasının mexanizmi və sintez şəraiti müzakirə olunub. Müdafiə laylı katalizatorların üst layında NiO miqdarı 2.5 %, qranulların içində isə beş dəfə az təşkil edir.

Açar sözlər: *müdafiə layı, kaolin, hidrotəmizləmə katalizatorları*